

AD

TECHNICAL REPORT ARCCB-TR-94049

THE ELECTRODEPOSITION OF LOW CONTRACTION CHROMIUM/MOLYBDENUM ALLOYS USING PULSE-REVERSE PLATING

MARK D. MILLER
STEPHEN LANGSTON



DECEMBER 1994



US ARMY ARMAMENT RESEARCH,
DEVELOPMENT AND ENGINEERING CENTER
CLOSE COMBAT ARMAMENTS CENTER
BENÉT LABORATORIES
WATERVLIET, N.Y. 12189-4050



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

19950329 095

DTIC QUALITY INSPECTED 1

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

The use of trade name(s) and/or manufacturer(s) does not constitute an official indorsement or approval.

DESTRUCTION NOTICE

For classified documents, follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For unclassified, limited documents, destroy by any method that will prevent disclosure of contents or reconstruction of the document.

For unclassified, unlimited documents, destroy when the report is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE December 1994		3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE THE ELECTRODEPOSITION OF LOW CONTRACTION CHROMIUM/MOLYBDENUM ALLOYS USING PULSE-REVERSE PLATING				5. FUNDING NUMBERS AMCMS: 6111.02.H611.1	
6. AUTHOR(S) Mark D. Miller and Stephen Langston					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Benét Laboratories, AMSTA-AR-CCB-O Watervliet, NY 12189-4050				8. PERFORMING ORGANIZATION REPORT NUMBER ARCCB-TR-94049	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Close Combat Armaments Center Picatinny Arsenal, NJ 07806-5000				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The use of modulated pulse periodic reverse (pulse-reverse) current to electrodeposit a low contraction (LC) chromium/molybdenum alloy has been evaluated. When using one full pulse-reverse plating cycle, the percent molybdenum in the deposit increased almost 400 percent (from 1 to 4 percent) as the current in the reverse cycle was increased from 0 to 10 amps. However, when the pulse-reverse current was carried to six full plating cycles, the percent molybdenum in the deposit was not dependent upon the current and remained constant at about 1 percent. This is about the same percent molybdenum that could be expected in direct current-plated LC chromium/molybdenum alloy and about half the percent molybdenum that could be expected in an on/off pulse-plated LC chromium/molybdenum alloy.					
14. SUBJECT TERMS Molybdenum, Chromium, Electroplating, Electrodeposition, Pulse, Pulse-Reverse				15. NUMBER OF PAGES 12	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

NSN 7540-01-280-5500

Standard Form 296 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
296-102

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	1
RESULTS	2
CONCLUSIONS	3
REFERENCES	4

List of Illustrations

1. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy.
One pulse-reverse cycle (with 0 amp on the reverse current) was used 5
2. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy.
One pulse-reverse cycle (with 1 amp on the reverse current) was used 6
3. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy.
One pulse-reverse cycle (with 5 amps on the reverse current) was used 7
4. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy.
One pulse-reverse cycle (with 10 amps on the reverse current) was used 8
5. The EDAX and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. Six pulse-reverse cycles (with 0, 1, 5, and 10 amps on the reverse current) were used 9

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to C. Rickard and A. Kapusta of Benét Laboratories for their metallographic data.

INTRODUCTION

The usefulness of existing high contraction (HC) chromium electrodeposits as well as future low contraction (LC) chromium electrodeposits is limited by the thermal resistance and the reactive environment found when using newer, high energy propellants. In addition, aqueous electrodeposition of refractory metals has typically been limited to just one metal--chromium (with a melting temperature of 1875°C). Therefore, the usefulness of both the present HC chromium and the future LC chromium coatings can be enhanced by raising their melting temperature by alloying them with other high melting temperature refractory metals such as molybdenum (with a melting temperature of 2600°C).

In addition, a chromium/molybdenum alloy electrodeposit is very desirable because of its reported benefits including improved wear, corrosion, and erosion resistance over conventional chromium deposits (refs 1-3). Yuan et al. have found that a chromium/molybdenum alloy electrodeposit possessed better tribological characteristics than pure chromium electrodeposits (ref 4). Brenner (ref 5) has reported that the chromium/molybdenum alloy did not have the network of cracks characteristic of the unalloyed chromium deposit and, in addition, the chromium/molybdenum codeposit lasted from three to eight times longer in wear tests than pure chromium deposits.

The molybdenum content in an aqueously deposited chromium/molybdenum alloy is usually quite low--no more than 1 percent. Investigators such as Ma (ref 6) claimed to have obtained chromium/molybdenum alloy deposits with molybdenum contents as high as 22 percent. However, attempts by Brenner (ref 5) and Holt (ref 7) to duplicate Ma's results were unsuccessful. More recent attempts to aqueously electrodeposit a direct current (dc)-plated chromium/molybdenum alloy with molybdenum contents higher than 1 percent have been unsuccessful (ref 8).

Molybdenum concentrations as high as 2.4 percent were obtained in an LC chromium/molybdenum alloy when unipolar (on/off) pulse current was used instead of straight dc current (ref 9). However, this is still not enough molybdenum to improve the thermal resistance or significantly improve the mechanical properties of the alloy. Recognizing the need to improve the molybdenum content beyond 2.4 percent, the use of pulse-reversing current was investigated.

EXPERIMENTAL PROCEDURE

The experimental procedure was carried out exactly as described in a previous report (ref 9) except for the electrodeposition process. Pulse reversing current was used instead of on/off pulse current. The LC Cr/Mo alloy was deposited using either one pulse-reverse cycle (total plating time 1350 seconds) or six pulse-reverse cycles (total plating time 8100 seconds). Each forward part of a pulse-reverse cycle consisted of a total time of 900 seconds (broken into 90 ms/90 ms on/off pulses). Each reverse part of a pulse-reverse cycle consisted of a total time of 450 seconds (broken into 1 ms/1 ms on/off pulses).

The current used for the forward part of a pulse-reverse cycle was kept constant at 10 amps (or 100 A/dm²). The current used for the reverse part of each pulse-reverse cycle was varied from 0 to 10 amps. The variation of the molybdenum content with increasing current during the reverse part of a cycle was evaluated.

RESULTS

The experiment was divided into two parts. In the first part, only one pulse-reverse cycle was used (for a total plating time of 1350 seconds). The current used for the reverse part of the cycle was varied from 0 to 10 amps (0 to 100 A/dm²). When the current for the reverse part of the cycle was at 0 amps, the molybdenum content in the LC chromium/molybdenum alloy was about 1 percent. The percentages are only approximations due to the limitations of doing quantitative measurements with energy dispersive x-ray analysis (EDAX). The results are shown in Figure 1. It is also obvious here that when the pulse-reverse cycle has 0 amps for the reverse current, the current profile resembles an on/off forward pulse.

Next, the reverse current was increased to 1 amp and the molybdenum content increased to about 2 percent. The results are shown in Figure 2. When the reverse current was then increased to 5 amps, the molybdenum content of the LC chromium/molybdenum alloy again increased--to about 3 percent (Figure 3). Finally, when the reverse current was increased to 10 amps, the percent molybdenum in the alloy increased to 4 percent. These results are shown in Figure 4. The plating thicknesses at these short pulse-reverse plating times never exceeded 5 μ m. This thickness is inadequate for gun-tube coatings which typically are 125 μ m thick.

However, the rise in the molybdenum content from 1 to 4 percent as the current in the reverse part of the cycle was increased from 0 to 10 amps is considered significant. Since the forward part of the cycle remained unchanged for this part of the experiment, this finding suggests that at higher reverse currents more chromium than molybdenum is being removed during the reverse part of the cycle. As a result, it could be concluded that it may be possible to increase the overall percent molybdenum beyond 4 percent simply by carrying out the plating times for several hours.

In the second part of the experiment, six pulse-reverse cycles were used in an effort to determine if the percent molybdenum in the chromium/molybdenum deposit could be increased beyond 4 percent simply by plating at longer times. The total plating time for the six pulse-reverse cycles was 8100 seconds. The current profile was identical to the first part of the experiment except that six pulse-reverse cycles were used instead of one.

The current used for the reverse part of each cycle was again varied from 0 to 10 amps. The results are shown in Figure 5. Unlike part one of the experiment, the molybdenum content of the chromium/molybdenum alloy did not increase as the reverse current was increased from 0 to 10 amps. The molybdenum content remained basically unchanged at about 1 percent. This observation leads to the conclusion that when using longer plating times (times long enough to get a deposit of at least 25 μ m), the molybdenum content of a chromium/molybdenum alloy cannot be improved beyond 1 percent when plating with pulse-reverse current.

CONCLUSIONS

The use of modulated pulse periodic reverse (or pulse-reverse) current was compared to dc and on/off pulse current with respect to increasing the molybdenum content of a aqueously plated chromium/molybdenum alloy. When using short plating times (one pulse-reverse cycle with a total plating time of 1350 seconds), a maximum molybdenum concentration of 4 percent was obtained. This compares to a maximum molybdenum concentration of 1 percent for dc-plated chromium/molybdenum alloys and 2.4 percent for on/off pulse-plated chromium/molybdenum alloys. However, the plating thicknesses at these short pulse-reverse plating times are inadequate (less than 5 μm) for gun-tube coatings which are typically 125 μm thick.

However, when six pulse-reverse cycles were used (in an effort to deposit thicker coatings), the maximum molybdenum concentration of the alloy was only 1 percent. This percentage is comparable to dc-plated chromium/molybdenum alloys and is significantly less than the 2.4 percent molybdenum obtained when using on/off pulse current.

REFERENCES

1. P. Fenton and A. Oolbekkink, Diesel Engineers and Users Association, June 1973.
2. K. S. Indira and B. Shenoi, "Electrodeposition of Chromium-Molybdenum Alloys," *Metal Finishing*, Vol. 63, 1965, pp. 56-79 and 94-97.
3. K. Aotani and K. Nistimoto, *J. Metal Finishing Society of Japan*, Vol. 21, No. 7, 1970, p. 356.
4. F. Bing, X. Fang, G. Wenzhen, Z. Yuan, and L. Yunfeng, "Tribological Characteristics of Cr-Mo Dispersed Electrodeposits," *Proceedings of the JSLE International Tribology Conference*, Tokyo, Japan, 1985.
5. A. Brenner, *Electrodeposition of Alloys*, Vol. II, 1st Ed., Academic Press, Inc., New York, 1963, p. 113.
6. Chuk Ching Ma (for Westinghouse Electric Corp.), "Electroplating of Chromium-Molybdenum Alloys," U.S. Patent No. 2526227, 1950.
7. M.L. Holt, "Less Common Metals and Alloys, Electrodeposition From Aqueous Solutions," *Metal Finishing*, Vol. 54, 1956, pp. 48-55.
8. Y.V. Pozdeeva, M.A. Shluger, and L.D. Tok, "Effect of Molybdate Ions on Electrodeposition of Chromium," *Prot. Met.*, Vol. 16, No. 3, March-April 1980, pp. 278-280.
9. Mark D. Miller and Stephen Langston, "Chromium/Molybdenum Alloy Plating Part I: The Electrodeposition of Low Contraction Chromium/Molybdenum Alloys Using Unipolar (On/Off) Pulse Plating," ARCCB-TR-94011, March 1994.

PULSE - REVERSING STUDY (with Cr/Mo)

ONE FULL CYCLE (900 sec foward/450 sec reverse)
 TOTAL PLATING TIME - 1350 sec (one full cycle)
 REVERSE CURRENT: 0 Amps

PULSE - REVERSING STUDY (WITH Cr/Mo) VARIATION IN REVERSE CURRENT

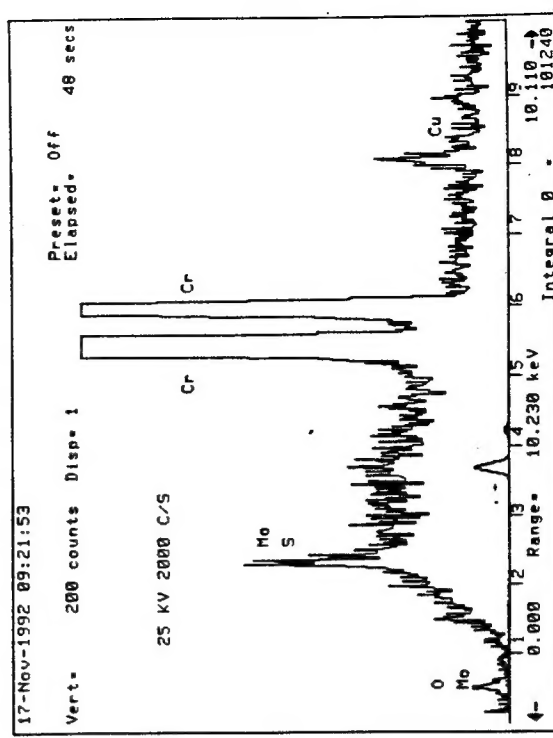
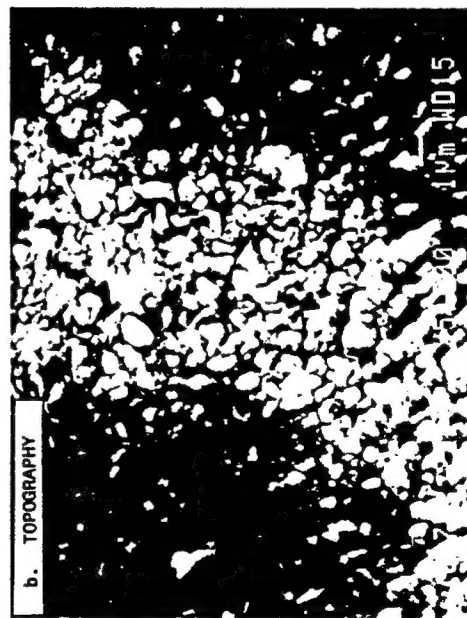
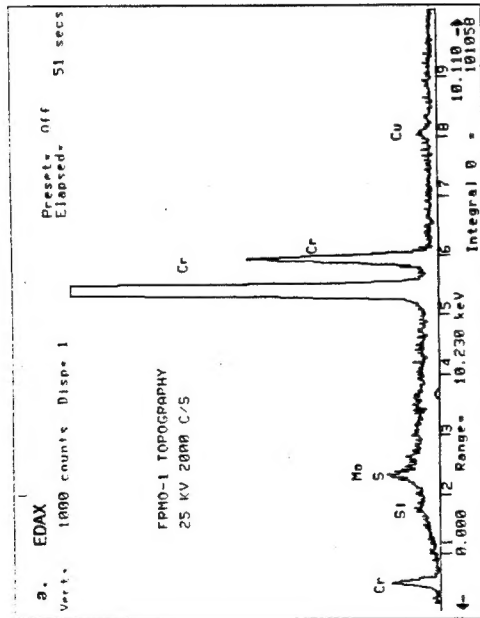
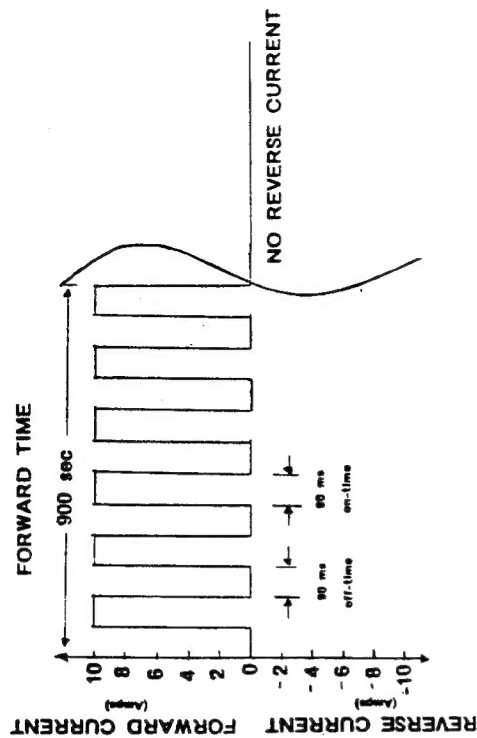
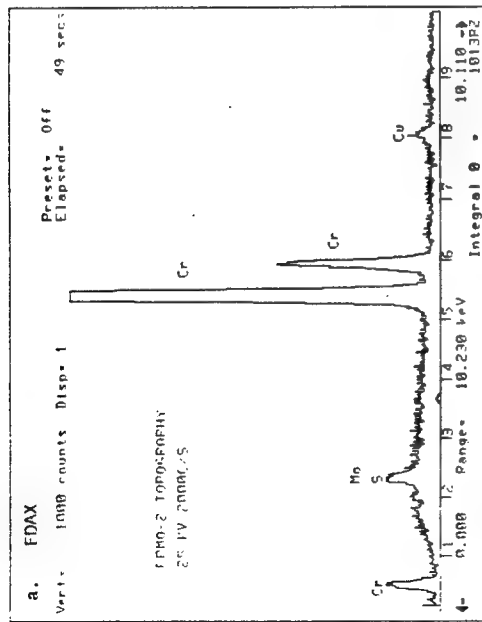


Figure 1. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 0 amps on the reverse current) was used.

PULSE - REVERSING STUDY (with Cr/Mo)
 ONE FULL CYCLE (900 sec forward/450 sec reverse)
 TOTAL PLATING TIME - 1350 sec (one full cycle)
 REVERSE CURRENT: 1 Amp



PULSE - REVERSING STUDY (WITH Cr/Mo)
 VARIATION IN REVERSE CURRENT

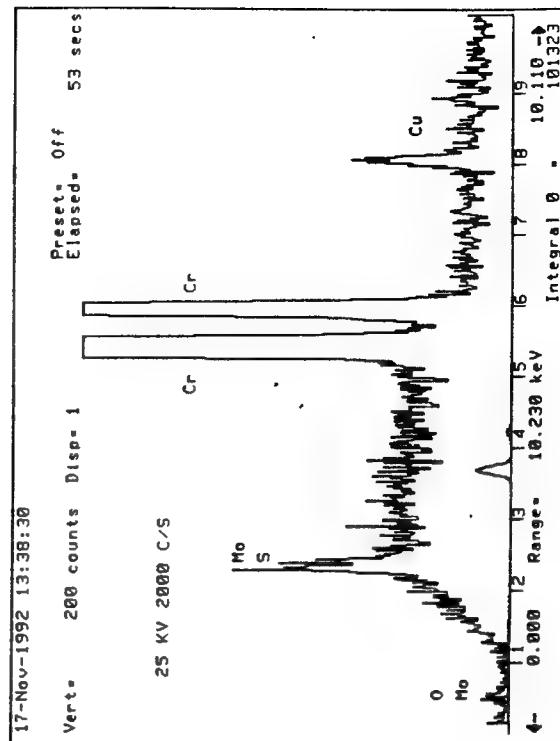
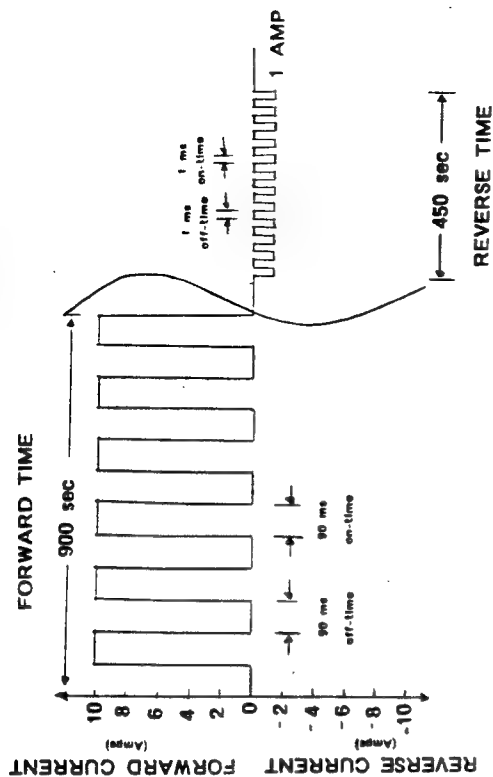
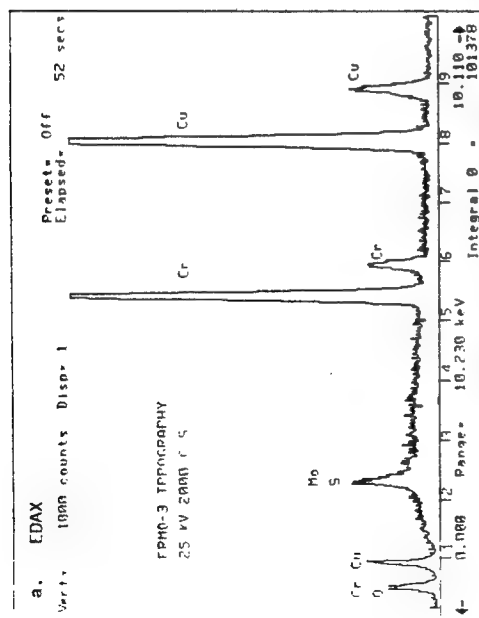


Figure 2. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 1 amp on the reverse current) was used.

PULSE - REVERSING STUDY (with Cr/Mo)

ONE FULL CYCLE (900 sec forward/450 sec reverse)
 TOTAL PLATING TIME - 1350 sec (one full cycle)
 REVERSE CURRENT: 5 Amps



PULSE - REVERSING STUDY (WITH Cr/Mo) VARIATION IN REVERSE CURRENT

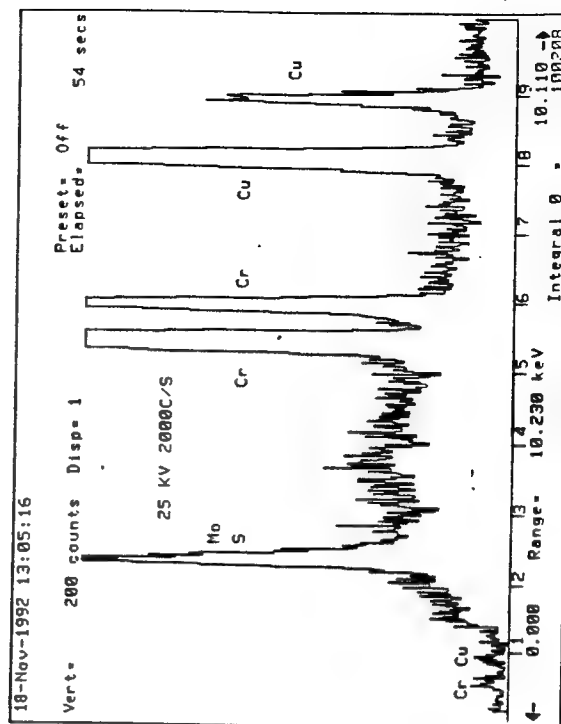
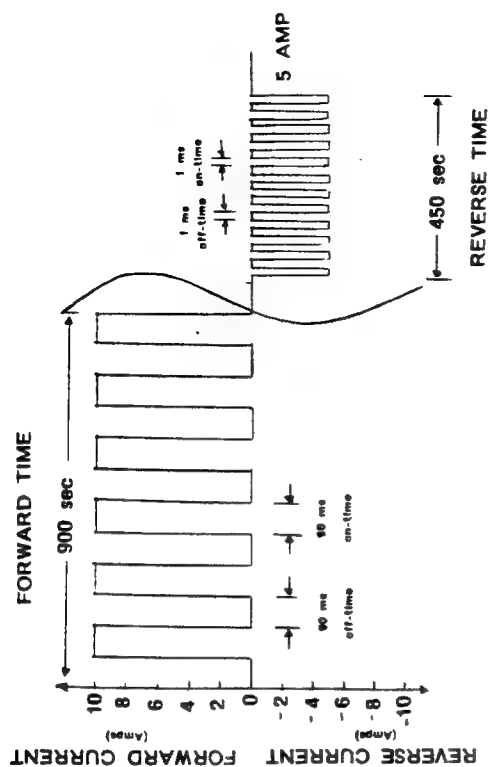
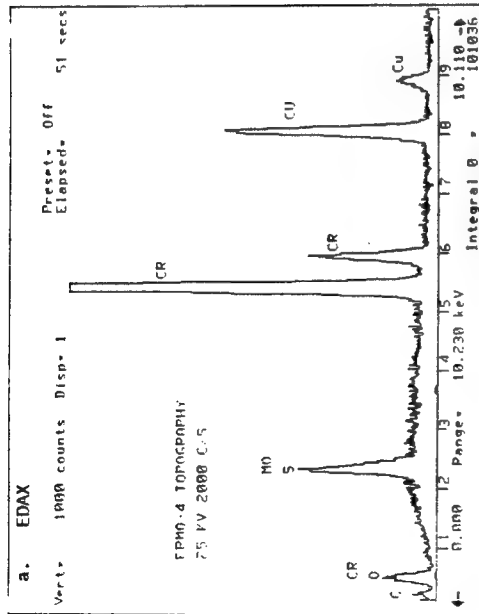


Figure 3. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 5 amps on the reverse current) was used.

PULSE - REVERSING STUDY (with Cr/Mo)

ONE FULL CYCLE (900 sec forward/450 sec reverse)
 TOTAL PLATING TIME - 1350 sec (one full cycle)
 REVERSE CURRENT: 10 Amps



PULSE - REVERSING STUDY (WITH Cr/Mo) VARIATION IN REVERSE CURRENT

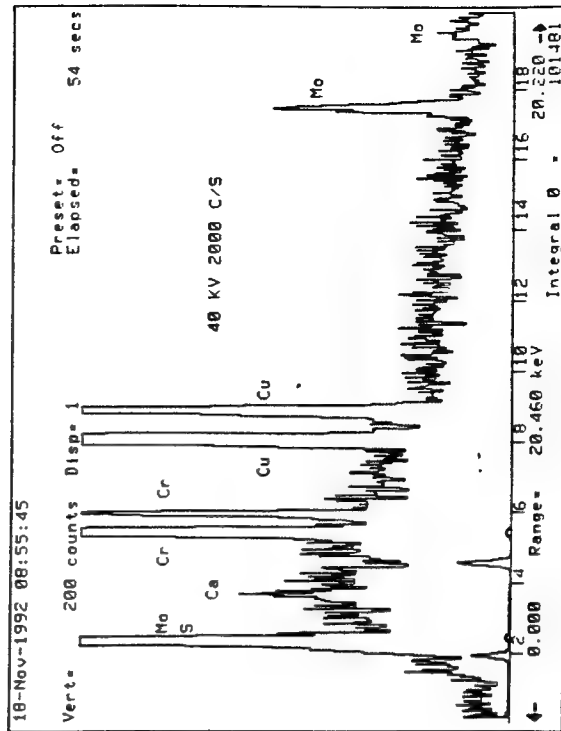
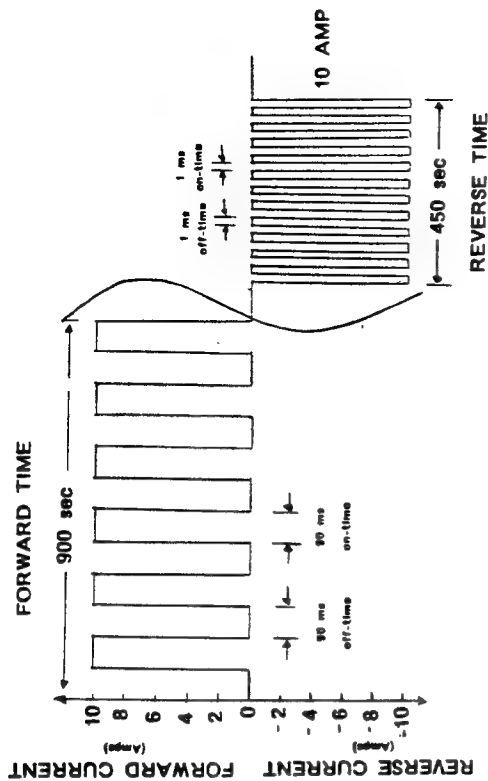
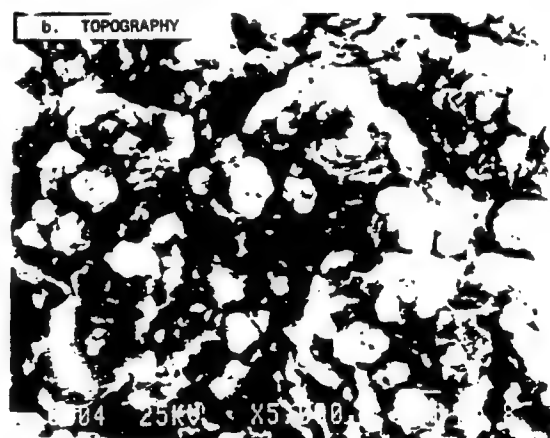
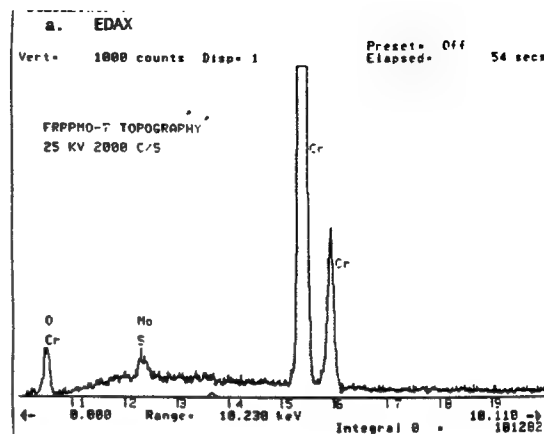
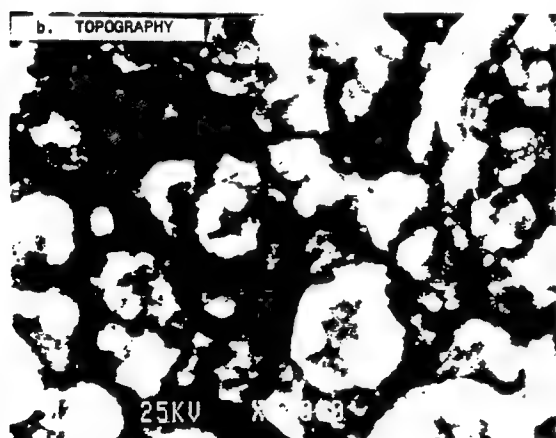
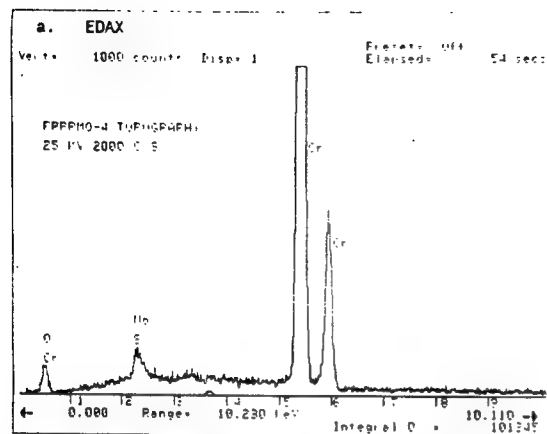


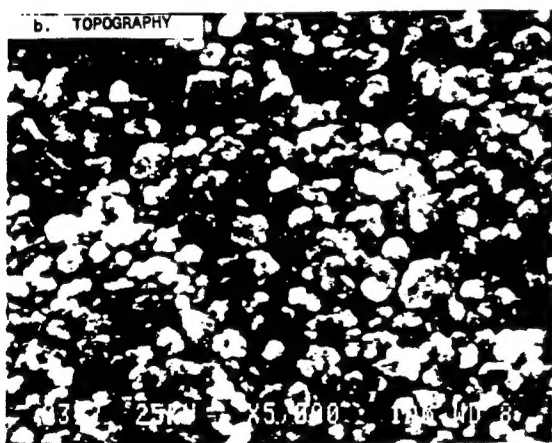
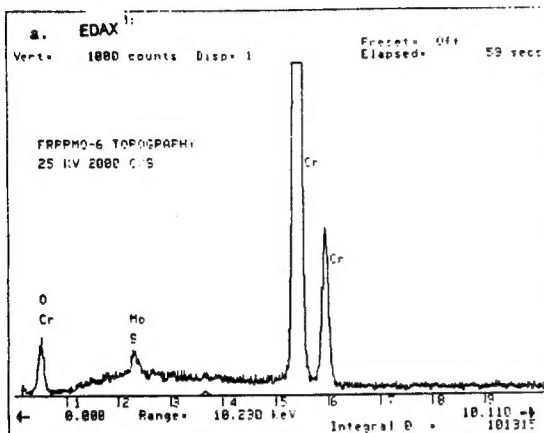
Figure 4. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 10 amps on the reverse current) was used.



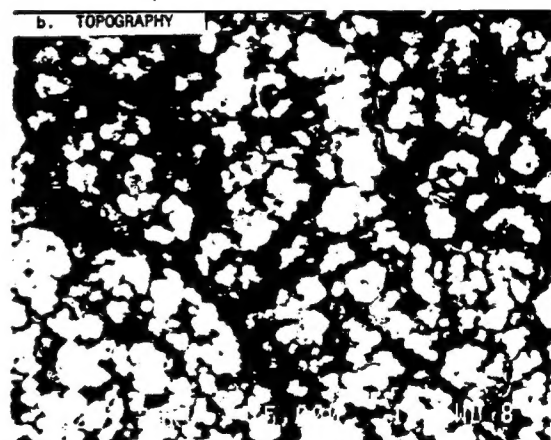
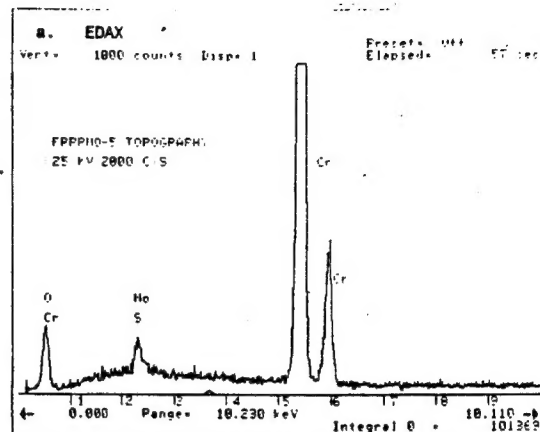
Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 0 Amp

Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 1 Amp

Figure 5. The EDAX and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. Six pulse-reverse cycles (with 0, 1, 5, and 10 amps on the reverse current) were used.



Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 5 Amps



Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 10 Amps

Figure 5. Continued.

TECHNICAL REPORT INTERNAL DISTRIBUTION LIST

	<u>NO. OF COPIES</u>
CHIEF, DEVELOPMENT ENGINEERING DIVISION	
ATTN: AMSTA-AR-CCB-DA	1
-DB	1
-DC	1
-DD	1
-DE	1
CHIEF, ENGINEERING DIVISION	
ATTN: AMSTA-AR-CCB-E	1
-EA	1
-EB	1
-EC	
CHIEF, TECHNOLOGY DIVISION	
ATTN: AMSTA-AR-CCB-T	2
-TA	1
-TB	1
-TC	1
TECHNICAL LIBRARY	
ATTN: AMSTA-AR-CCB-O	5
TECHNICAL PUBLICATIONS & EDITING SECTION	
ATTN: AMSTA-AR-CCB-O	3
OPERATIONS DIRECTORATE	
ATTN: SMCWV-ODP-P	1
DIRECTOR, PROCUREMENT & CONTRACTING DIRECTORATE	
ATTN: SMCWV-PP	1
DIRECTOR, PRODUCT ASSURANCE & TEST DIRECTORATE	
ATTN: SMCWV-QA	1

NOTE: PLEASE NOTIFY DIRECTOR, BENÉT LABORATORIES, ATTN: AMSTA-AR-CCB-O OF ADDRESS CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST

	<u>NO. OF COPIES</u>		<u>NO. OF COPIES</u>
ASST SEC OF THE ARMY RESEARCH AND DEVELOPMENT ATTN: DEPT FOR SCI AND TECH THE PENTAGON WASHINGTON, D.C. 20310-0103	1	COMMANDER ROCK ISLAND ARSENAL ATTN: SMCRI-ENM ROCK ISLAND, IL 61299-5000	1
ADMINISTRATOR DEFENSE TECHNICAL INFO CENTER ATTN: DTIC-OCF (ACQUISITION GROUP) BLDG. 5, CAMERON STATION ALEXANDRIA, VA 22304-6145	12	MIAC/CINDAS PURDUE UNIVERSITY P.O. BOX 2634 WEST LAFAYETTE, IN 47906	1
COMMANDER U.S. ARMY ARDEC ATTN: SMCAR-AEE	1	COMMANDER U.S. ARMY TANK-AUTMV R&D COMMAND ATTN: AMSTA-DDL (TECH LIBRARY) WARREN, MI 48397-5000	1
SMCAR-AES, BLDG. 321	1	COMMANDER U.S. MILITARY ACADEMY ATTN: DEPARTMENT OF MECHANICS WEST POINT, NY 10966-1792	1
SMCAR-AET-O, BLDG. 351N	1		
SMCAR-FSA	1		
SMCAR-FSM-E	1		
SMCAR-FSS-D, BLDG. 94	1		
SMCAR-IMI-I, (STINFO) BLDG. 59	2	U.S. ARMY MISSILE COMMAND REDSTONE SCIENTIFIC INFO CENTER ATTN: DOCUMENTS SECTION, BLDG. 4484 REDSTONE ARSENAL, AL 35898-5241	2
PICATINNY ARSENAL, NJ 07806-5000			
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-DD-T, BLDG. 305 ABERDEEN PROVING GROUND, MD 21005-5066	1	COMMANDER U.S. ARMY FOREIGN SCI & TECH CENTER ATTN: DRXST-SD 220 7TH STREET, N.E. CHARLOTTESVILLE, VA 22901	1
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-WT-PD (DR. B. BURNS) ABERDEEN PROVING GROUND, MD 21005-5066	1	COMMANDER U.S. ARMY LABCOM MATERIALS TECHNOLOGY LABORATORY ATTN: SLCMT-IML (TECH LIBRARY) WATERTOWN, MA 02172-0001	2
DIRECTOR U.S. MATERIEL SYSTEMS ANALYSIS ACTV ATTN: AMXSY-MP ABERDEEN PROVING GROUND, MD 21005-5071	1	COMMANDER U.S. ARMY LABCOM, ISA ATTN: SLCIS-IM-TL 2800 POWER MILL ROAD ADELPHI, MD 20783-1145	1

NOTE: PLEASE NOTIFY COMMANDER, ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER,
BENÉT LABORATORIES, CCAC, U.S. ARMY TANK-AUTOMOTIVE AND ARMAMENTS COMMAND,
AMSTA-AR-CCB-O, WATERVLIET, NY 12189-4050 OF ADDRESS CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST (CONT'D)

	<u>NO. OF COPIES</u>		<u>NO. OF COPIES</u>
COMMANDER		WRIGHT LABORATORY	
U.S. ARMY RESEARCH OFFICE		ARMAMENT DIRECTORATE	
ATTN: CHIEF, IPO	1	ATTN: WL/MNM	1
P.O. BOX 12211		EGLIN AFB, FL 32542-6810	
RESEARCH TRIANGLE PARK, NC 27709-2211			
DIRECTOR		WRIGHT LABORATORY	
U.S. NAVAL RESEARCH LABORATORY		ARMAMENT DIRECTORATE	
ATTN: MATERIALS SCI & TECH DIV	1	ATTN: WL/MNMF	1
CODE 26-27 (DOC LIBRARY)	1	EGLIN AFB, FL 32542-6810	
WASHINGTON, D.C. 20375			

NOTE: PLEASE NOTIFY COMMANDER, ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER,
BENÉT LABORATORIES, CCAC, U.S. ARMY TANK-AUTOMOTIVE AND ARMAMENTS COMMAND,
AMSTA-AR-CCB-O, WATERVLIET, NY 12189-4050 OF ADDRESS CHANGES.
